1911
B17

BAKER

Compounds of Yttrium

Chemistry

M. S.

1911

UNIV. OF
ILLINOIS
LIBRARY

UNIVERSITY OF ILLINOIS
LIBRARY

Class 1911
Book B17
Volume

Digitized by the Internet Archive
in 2013

http://archive.org/details/compoundsofyttri00bake

938
C
[illegible]

COMPOUNDS OF YTTRIUM

BY

CLARENCE JAMES BAKER
A. B. University of Denver, 1907

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1911

1911
B17

1911
B17

UNIVERSITY OF ILLINOIS

THE GRADUATE SCHOOL

May 30, 1911.

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

CLARENCE JAMES BAKER

ENTITLED COMPOUNDS OF YTTRIUM

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE

Clarence W. Balke
In Charge of Major Work

W. A. Noyes
Head of Department

Recommendation concurred in:

Committee
on
Final Examination

197537

UIUC

COMPOUNDS OF YTTRIUM.

INTRODUCTION

The compounds described in this paper were obtained in connection with a more extensive investigation of the rare earths,one phase of which involves a search for new methods or compounds which may improve the present methods used for the separation of these elements. The methods already in use for this purpose may be divided into two large divisions: Fractional Precipitation and Fractional Crystallization. Of these the latter is to be preferred because it is possible to carry out a larger number of recrystallizations with less loss of material than is the case with fractional precipitation. It is highly desirable to find new compounds which will give a more rapid separation than can be accomplished by those now in use. With this point in mind a number of new compounds of Yttrium have been prepared in connection with the extraction of Yttrium material and the preliminary separation of the earths by methods already in use.

PREPARATION OF YTTRIUM MATERIAL

The yttrium oxide used in the preparation of these salts was prepared from a mixture of the rare earth oxalates from the mineral Xenotime

which was obtained from Dr. G. P. Drossbach and Co. of Germany. This mixture consisted of the oxalates of both the cerium and yttrium groups. In working up the material, the members of the cerium group were separated by precipitation as double sodium sulphates in a saturated solution of sodium sulphate. The yttrium earths were precipitated from the filtrate by the addition of oxalic acid. The resulting oxalate was washed thoroughly, dried and converted into the sulphate by evaporation and ignition with sulphuric acid. This salt was dissolved in ice cold water and the yttrium earths again precipitated as oxalates. The latter were then washed in order to remove the last traces of sodium salts. The oxalates were once more converted into the sulphates and heated to remove all excess of sulphuric acid. The earths were next converted into the bromates by double decomposition with barium bromate[1] and the latter was then subjected to a long fractional crystallization. Those fractions richest in yttrium obtained by this method were subjected to further purification by means of the chromate method[2] as follows. Eighty grams of the yttrium oxide was mixed with 160 grams of chromic anhydride, the mixture dissolved in two liters of water and boiled with the addition of steam for two hours during which time five hundred cubic centimeters of a ten per cent solution of potassium chromate was gradually added from a dropping funnel. After the addition of the chromate the boiling was continued for two hours more and the resulting precipitate was filtered off. To the filtrate was added a fresh portion of five hundred cubic centimeters of potassium chromate, drop by drop, and the boiling was continued as before until a second fraction had been precipitated. The temperature

---

[1] James; Jour.Am.Chem.Soc. 30, 182 and 979.
[2] Mäthmann and Bohn; Ber. 33, 42-9.

was so regulated that the volume of the boiling liquid remained constant throughout the operation. After filtering out the second fraction the boiling was continued with the addition of potassium chromate as described, until six fractions had been removed. The last traces of yttrium were recovered by the evaporation of the resultant mother liquor, which was then boiled with potassium hydroxide to convert the chromium into potassium chromate, to be used again with fresh material. The boiling was carried out in five-liter Jena flasks--- a tier of eight flasks being run simultaneously. The first three fractions were set aside and returned to the process. The middle fraction was shown to have about the same composition as the original substance and subsequent fractions showed a steady increase in the purity of the yttrium. The material recovered from the final mother liquor was the best which was secured by this method. The last fractions obtained were separated out, converted to the oxalates and twice reprecipitated to remove the last traces of chromium. The final precipitate after being carefully ignited in a platinum crucible was found to be perfectly white in color, which may be taken as an indication of its high degree of purity. On being converted into the chloride and examined by means of the spectroscope in a saturated solution, it was found to be entirely free of all absorption lines with the exception of a very few extremely faint erbium lines.

DOUBLE SULPHATES OF YTTRIUM

The sulphates and double sulphates of yttrium have been used in the determination of the atomic weight of this element very successfully. Determinations made up to the year 1873 were so widely variant in results and

were made on material which has since been shown to be so impure that they are of but little value. Cleve and Hoglund[1] seem to have obtained the purest material up to their time. By converting the oxide into the sulphate they found $Y=89.58$. In a later determination (1883) Cleve[2] obtained 89.1 as the atomic weight. This value has been found by Jones[3] to be a little too high and the present weight is now taken as 89.

The following double sulphates were prepared by Cleve:[4]

$Y_2(SO_4)_3.4K_2SO_4$

$2Y_2(SO_4)_3.3K_2SO_4$

$Y_2(SO_4)_3.Na_2SO_4.2H_2O$

$Y_2(SO_4)_3.2(NH_4)_2SO_4.9H_2O$.

CAESIUM YTTRIUM DOUBLE SULPHATE

$Cs_2SO_4.Y_2(SO_4)_3.8H_2O$

By mixing a saturated solution of caesium sulphate and yttrium sulphate in about equi-molecular proportions and allowing the solution to evaporate spontaneously to crystallization, beautiful white crystals separated which were found to have the composition indicated above. The crystals were thoroughly dried between filter paper and a sample was prepared for analysis by grinding a portion in an agate mortar. The water of hydration was determined by heating over a low Bunsen flame to a temperature somewhat below red heat, in a platinum crucible on wire gauze, until a constant weight was obtained. The dry sample was then dissolved in two hundred cubic centi-

---

[1] Bihang.till.Vet.Ask.Handl. 1873 1 III No.8.
[2] Bull.Soc.Chim. 39, 120.
[3] Am.Chem.Jour. 17, 154.
[4] Bull.Soc.Chim. (2) 18, 193, 289.

meters of water and a few drops of hydrochloric acid added. The yttrium was precipitated from this solution while warm by the addition of slightly more than the calculated quantity of oxalic acid. Care was taken to have both the solution and the acid hot when mixed in order that the precipitate obtained might be granular. The precipitate was allowed to stand over night before filtering, in order to insure complete precipitation, then filtered, washed, ignited and weighed as the oxide of yttrium. The filtrate was evaporated to dryness in a platinum crucible and the residue ignited with two or three drops of sulphuric acid, to expel the excess of oxalic acid, and finally weighed as caesium sulphate. Sulphur trioxide was determined in another sample by precipitation with barium chloride in the usual way. The following analytical results were obtained:

THEORY		FOUND
23.25 %	Y_2O_3	23.52 %
29.01	Cs_2O	29.80
32.92	SO_3	33.07
14.35	H_2O	14.81

RUBIDIUM YTTRIUM DOUBLE SULPHATE

$Rb_2SO_4.Y_2(SO_4)_3.8H_2O$

This salt, prepared and analyzed in the manner just described for the caesium salt gave the following results on analysis:

THEORY		FOUND
25.80 %	Y_3O_3	25.85 %
21.23	Rb_2O	20.73
36.53	SO_3	36.73
16.43	H_2O	16.21

SODIUM YTTRIUM DOUBLE SULPHATE

$Na_2SO_4.Y_2(SO_4)_3.3H_2O$

The double sodium sulphate prepared by Cleve is described as a white amorphous powder. During the present work a mixture of a saturated solution of sodium sulphate and yttrium sulphate was allowed to concentrate by spontaneous evaporation to crystallization, as in the preceding salts. This salt was analyzed in the same manner as described for the caesium salt and gave the following results:

THEORY		FOUND
28.10 %	Y_2O_3	27.92 %
15.42	Na_2O	16.57
49.75	SO_3	49.26
6.73	H_2O	7.08

TRI-CHLOR-ACETATE

$Y(C_2Cl_3O_2)_3$

The yttrium salts of organic acids have not been as yet very fully investigated. Perhaps the most extensive research concerning the rare earth salts of the organic acids, which has so far been undertaken, is that carried out by Erdmann and Wirth.[1]

During the present work a number of compounds such as the buterate, lactate and tri-chlor-acetate were prepared. The first two were found to be very difficultly soluble bodies, formed by the addition of yttrium chloride to the particular acid in question. Yttrium tri-chlor-acetate was made by dissolving yttrium oxide in tri-chlor-acetic acid, and allowing the solution to crystallize by spontaneous evaporation. This salt was found to hydrolize

---

[1] Leib. Ann. 361, 190.

strongly, so that it was necessary to have a large excess of trichloracetic acid in the solution, and for the same reason it was impossible to evaporate the solution on the water bath. The salt separated as beautiful white needles which were found to be anhydrous. They did not lose weight on being heated for several hours in the water oven. The yttrium was determined in the usual way with the following result:

THEORY		FOUND
19.60 $^0/_0$	Y_2O_3	19.62 $^0/_0$

In conclusion it may be said that work is under way on the double selenates and tellurates of yttrium.

o o o o o o

I wish to take this opportunity to express my thanks to Dr. C.W. Balke for his kindly assistance, careful direction and untiring patience during the progress of this work.

UNIVERSITY OF ILLINOIS-URBANA
3 0112 086826978